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Geochemical Alteration of Backfill: FY 98 Status Report

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Lawrence Livermore National Laboratory

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Introduction

The Yucca Mountain Project is considering some type of backfill, possibly emplaced as a capillary barrier, for inclusion in the Engineering Barrier System (EBS) at the potential Yucca Mountain nuclear waste repository site. The performance of capillary barriers in isothermal, low-temperature, environments has been studied extensively (e.g., *Ho and Webb*, 1998; *Oldenburg and Pruess*, 1993; *Ross*, 1990). The performance of capillary barriers in an non-isothermal, high temperature environment, such as during the thermal pulse phase of a nuclear waste repository, has received much less attention. One concern is that the backfill materials may be altered from that of the as-placed material by the hydrothermal regime imposed by the emplacement of waste in the repository, changing hydrologic properties in a way that degrades the performance of the EBS system. This report is a status report on our efforts to address this concern. The work was initiated by SCR #98-76-041 and was authorized to begin at LLNL in summer 1998.

This report is organized as follows. In the first part, we discuss our understanding of the relevant issues of backfill performance based on thermal hydrology. We focus here on changes to hydrologic properties, but we recognize that changes to thermal, mechanical and chemical (e.g., sorptive) properties are also important. Our primary interest is in addressing concerns over possible changes in the magnitude of key hydrologic properties (i.e., porosity, permeability, and moisture retention characteristics) that could significantly affect the design performance of backfill in the EBS. We report on what we know from previous work about geochemical alteration of backfill material, focusing primarily on crushed tuff. In the second part of this report, we present our progress on geochemical studies on backfill materials. These include sub-boiling, two-phase column experiments, batch experiments at above boiling temperatures and associated numerical modeling activities.

Background

Thermal-Hydrological Behavior of EBS with Backfill

One of the primary purposes of using granular backfill (e.g., crushed tuff, sand) in the EBS is to minimize water contact to the waste packages. Water contact on waste packages can occur either as liquid-phase flow from seepage or capillary-driven wicking into and through the drift, or condensation of water vapor. Condensation of water vapor onto waste packages depends on the relative humidity (RH) on the waste package, which in turn depends on the relative humidity at the drift wall, the temperature difference between the waste package and the drift wall, and the liquid-phase flux reaching the waste package. Condensation of water vapor also depends on the presence and relative abundances of any salts that may have formed on the waste package surfaces due to the hygroscopic behavior of certain salts.

There are two major ways in which granular backfill helps to minimize liquid-phase flow onto waste packages. The first is its role as a thermal barrier. Thermal barriers minimize water contact onto waste packages by keeping the near-field environment hotter and less humid for a longer period of time. The second is its role as a capillary barrier. Capillary barriers consist of two layers of backfill materials with a sloping interface between the layers, and utilize the contrast in capillarity between the layers to keep the liquid in the upper layer. Based on these barrier concepts, many backfill designs have been considered within the Yucca Mountain Project, including a single layer of crushed tuff backfill and capillary barriers with various combinations of materials.

The hydrological properties that determine the effectiveness of backfill performance include saturated (i.e., intrinsic) permeability; the relationship between permeability, saturation and capillary pressures; and porosity. The relationship of these other properties to porosity is determined by grain size and sorting. In general, fine-grained, poorly sorted materials retain more moisture at a given capillary pressure than coarse-grained, well sorted materials.

The moisture retention characteristics and relative permeability of a porous material are often described by van Genuchten parameters α and m (*van Genuchten*, 1980). Small α values indicate that water is easily imbibed by the material and that, conversely, a relatively high pressure is required for water to drain out of the material. The m parameter reflects the pore size distribution. In a partially saturated material, permeability is a function of both intrinsic permeability of a material and its saturation. A low m value indicates a material that has relatively larger changes in permeability for a given change in saturation. In backfill materials with nonporous grains, only intergranular porosity is important, whereas in backfill with porous grains, such as crushed tuff, both intergranular and intragranular porosity are important.

The permeability of backfill is important to the performance of the EBS for two reasons. The first concerns the flow capacity of the upper layer of a two-layer capillary barrier. A key issue for the performance of a capillary barrier is whether reduction of permeability in the upper layer would be enough to diminish the capacity of the upper layer to divert incoming seepage or to cause a "vapor lid" whereby buoyant vapor flow would be trapped, then condense and drain onto waste packages. A second concern is that an increase in permeability would increase vapor convection in the backfill enough so that its effectiveness as a thermal barrier is decreased.

The moisture retention characteristics of backfill determine how much any incoming, localized seepage flux remains localized. Some degree of spreading throughout the upper layer of a capillary barrier due to capillary forces is desirable to minimize the possibility for localized flux exiting the bottom of that layer. The contrast in moisture retention characteristics between the upper and lower layers of a capillary barrier is also important. In a capillary barrier, it is the contrast between large capillarity in the upper layer relative to that in the lower layer that keeps water in the upper layer from entering the lower layer. Similarly, the contrast in moisture retention characteristics between backfill and the drift wall is important to minimize wicking of moisture from the drift into the backfill in contact with the drift wall.

The magnitude of changes in hydrologic properties which constitute a significant concern, the timing of changes throughout the performance period, and the importance of bulk property changes versus localized changes (perhaps at the boundary of the upper and lower layers of a capillary barrier), have not been adequately addressed. Small changes (e.g., precipitation of material at grain-to-grain contacts) at certain times for some materials and designs may significantly reduce EBS performance. In other cases, changes in hydrologic properties may by unimportant or improve performance. For example, replacement of one mineral type by another without changing the inter- or intra-particle porosity would not necessarily affect hydrologic performance (although radionuclide-sorptive properties could be impacted). We plan to investigate the sensitivity of backfill performance to hydrologic properties and the effect of coupled thermal-hydrological-chemical changes on backfill performance through numerical modeling activities next fiscal year.

Geochemical Alteration of Backfill Materials

Hydrothermal experiments with crushed, devitrified, repository-equivalent, Topopah Springs tuff provide us with information on expected geochemical alteration of this material. The mineralogy of this tuff is dominated by cristobalite, alkali feldspar, and quartz, which together comprise 98 % (by volume) of the rock; minor plagioclase, smectite, and biotite define the remaining fraction (*Warren et al.*, 1984; *Delany*, 1985).

Alteration under saturated conditions – *Knauss et al.* (1985) conducted a series of hydrothermal experiments in which this Topopah Springs tuff was reacted with synthetic J-13 well water (*Harrar et al.*, 1990) at 90°C, 150°C, and 250°C for up to 66 days in single-phase batch reactors. In the 250°C (pressurized) run, the primary alteration products were the Ca-rich, mordenite-type zeolite, dachiardite, mordenite itself and minor cristobalite and Ca-rich clay. In the 150°C run only the (presumed) cristobalite was observed, while no alteration products were observed in the 90°C experiment. *Knauss et al.* (1987) conducted similar experiments with the same materials at 90°C and 150°C, but for 303 days. Dachiardite was observed in the 150°C run, but no alteration products were identified in the 90°C run. The most prominent change in the water chemistry in these systems was the increase in the concentration of aqueous silica, which appeared to be controlled by cristobalite solubility.

Single-phase column experiments using this same Topopah Springs tuff at 240°C with deionized water were conducted more recently (*Johnson et al.*, 1998). Scanning Electron Microscope (SEM) images of the post-test tuff grains clearly illustrate striking evidence of feldspar and silica dissolution, the extent of which varied from pervasive near the fluid inlet to incipient near the outlet. The only evidence of alteration minerals found was two volumetrically-minor phases observed close to the column outlet. The first of these was a silica polymorph occurring as isolated 10-30 μm diameter spheres, morphologically identical to the secondary cristobalite produced by interaction at 250°C by *Knauss et al.* (1985). The second alteration phase occurred as submicron size crystals lying on primary-mineral surfaces and was morphologically similar to the Ca-rich clay observed by *Knauss et al.* (1985).

These column experiments were modeled using a reactive transport code called GIMRT (*Steefel and Yabusaki*, 1995). Assuming that in addition to the starting minerals (alpha-cristobalite, K-feldspar, quartz, albite and anorthite), the only possible secondary minerals were amorphous SiO_2, paragonite, muscovite, kaolinite, pyrophyllite, and aluminous oxide/hydroxides (gibbsite, diaspore, and boehmite), good correspondence between physical and computational model were obtained (*Johnson et al.*, 1998). In agreement with the post-mortem examination, the bulk of the column displayed evidence of dissolution and only minor precipitation near the outlet. The calculations show an increase of 25-50% in porosity in the first few centimeters of the column and very small or no changes in the rest of the column. Although no post-test porosity measurements were made, these predicted porosity changes are consistent with post-test SEM observation. No measurements of permeability were made in any of the experiments described above.

Alteration under unsaturated conditions – Based on the assumption that aqueous chemical reactions occurring in adsorbed water are similar to those occurring in a bulk solution, alteration of minerals, rocks, and glasses under unsaturated conditions is thought to be similar to alteration under saturated conditions. In a broad sense, this hypothesis has been borne out by observations related to the alteration of waste form glasses and tuff samples under fully saturated and 100% relative humidity air conditions (*Abrajano et al.*, 1990; *Knauss and Beiriger*, 1984). A major difference between unsaturated and saturated alteration experiments and/or scenarios is the relative proportion of solid to solution. In the case of unsaturated conditions, the extent of dissolution of the solid required to raise the concentration of dissolved species in the small amount of water in the adsorbed film is very small. Hence, the time for the solution to reach saturation (i.e., a concentration level where any one mineral precipitates) with minerals in the rock, or potential secondary phases, is much shorter than for an equivalent saturated test where the water to rock ratio is much larger. On the other hand, because the mass of solution to rock is so small in the unsaturated case, the extent of dissolution of the rock prior to reaching equilibrium is orders of magnitude smaller. This implies that the alteration of materials for unsaturated conditions may be restricted to the surfaces of nonporous granular material or mineral grains within porous granular material. In theory, even under unsaturated conditions, alteration will continue until all of the solid is converted to the phases that are most stable at the temperature, pressure, and relative humidity (assuming that water is not limiting) in question.

Because of the difficulty in measuring the composition of adsorbed solutions, an assessment of the mineralogical changes observed in alteration experiments is difficult. *Bruton and Viani* (1992) showed using geochemical modeling, that because of the lowered water activity imposed by a lowered relative humidity, the phases predicted to form from reaction of Topopah Spring tuff with a J-13 type groundwater differed from those predicted for an equivalent modeling run at a water activity near unity (i.e., fully saturated condition). In the fully saturated case, mica, clinoptilolite and smectite were predicted to form; in the unsaturated case (p/p° 0.8) a less hydrated assemblage was predicted to form — albite, stilbite, and smectite.

Previous experimental observations of the alteration of Yucca Mountain tuffs, as well as other materials, at elevated temperatures have shown that for relative water vapor pressures, p/p°, above about 0.6-0.7 (i.e., relative humidity 60-70%), chemical and mineralogical alteration is measurable on time scales of weeks to months (*Abrajano et al.*, 1986; *Abrajano et al.*, 1989; *Fyfe*, 1976; *Knauss and Beiriger*, 1984; *Papadakis et al.*, 1991). At lower relative vapor pressures, the specific point being material dependent, chemical alteration of the material becomes negligible.

Reflux conditions –Rimstidt et al. (1989) and *Rimstidt and Williamson* (1991) report results of two-phase, reflux experiments with crushed Topopah Springs tuff. They used a 1-2 mm size fraction of crushed tuff (fines removed). The experimental apparatus consisted of a 61 cm long vertical reactor with a volume of about 5 liters, partially filled with water, a heating assembly at the base, a cooling assembly at the top and a vapor escape port near the top open to the atmosphere. During the approximately month-long experiment, boiling took place at the base, water vapor rose to the top, condensed and flowed downward toward the base where it boiled again. The system was connected to an external water reservoir which was used to maintain a constant liquid level in the experiment. Several different water compositions were used in the experiments, including deioinized water, a 0.125 NaCl solution and a synthetic J-13-like well water.

The authors report that post-test SEM observations revealed extensive mineral dissolution throughout the top of the system. Opaline silica and iron oxides and hydroxides precipitated in the upper part of the column. The bottom of the system showed extensive mineral precipitation including silica, iron oxyhydroxides, stilbite and possibly clay. A layer of rock grains cemented with amorphous silica formed at the face of the heater assembly. No hydrologic property measurements were reported. Because there was no way to observe actual flow paths, and thermal-hydrological-chemical behavior is complex, it is difficult to quantify these experimental results for use in predictive reactive transport models.

Another relevant experiment consisted of wafers of tuff suspended over a reservoir of J-13 groundwater at 100% relative humidity and 150 °C (*Knauss and Beiriger*, 1984). It was assumed that under the conditions of the experiment, condensation of water on the tuff wafer and subsequent dripping into the reservoir below (i.e., refluxing), probably occurred. Little in the way of secondary mineral formation was observed (with the exception of calcite, which may have been due to loss of CO_2 during the experiment).

Alteration of sand backfill – Because of the low solubility of quartz, if a dominantly quartz sand is used as a backfill, the chemical and mineralogical alteration expected under humid elevated temperature conditions would be expected to be less than that of Topopah Spring tuff. To the degree that sands may contain other phases besides quartz, such as feldspars, rock fragments, or fine particles adhering to larger particle surfaces, some mineralogic reaction would probably occur even for sand.

Previous Efforts to Evaluate Geochemical Effects

A recent study by *Zhou et al.* (1996) considered possible geochemical changes in crushed tuff due to coupled thermal-hydrological-chemical changes in a potential repository at Yucca Mountain and concluded that significant impacts on EBS performance would be unlikely. *Zhou et al.* (1996) study report on a geochemical modeling calculation to estimate potential porosity changes due to mineral precipitation that could be generated by a boiling front propagating through a layer of crushed tuff. The authors use the EQ3/6 computer code (*Wolery*, 1992) to simulate changes in reactant and alteration minerals in a batch system as heating raises the temperature in a volume of crushed tuff from 18°C to 100°C at a rate estimated from thermal-hydrological modeling. Both a closed system, where the composition of the gas phase is buffered by water-rock interaction, and an open system, where the gas composition is externally controlled, were considered. The authors conclude that the resultant molar volume changes, and therefore any porosity changes, are insignificant.

Zhou et al. (1996) also report on calculations of porosity changes due to the evaporation of pore water to complete dryness. Both J-13 well water and a pore water in the unsaturated zone at Yucca Mountain were considered in the *Zhou et al.* (1996) analysis. The total volume of precipitates predicted to form from J-13 water and unsaturated pore water are reported as 0.11 and 1.0 cm^3/kg H_20, respectively. Many of the minerals that precipitate when the solution is taken to complete dryness are highly soluble and would dissolve almost immediately upon rewetting so these low estimates of total porosity change are conservative. The authors conclude that changes in porosity are not likely to be significant given the large volumes of water that would be needed to precipitate volumes of minerals significant enough to allow cementation of the backfill to the extent that cracks would form.

We offer the following comments regarding the conclusions of *Zhou et al.* (1996) that geochemical changes are not likely to be significant to EBS performance. If water were allowed to flow, and minerals therefore allowed to dissolve in one place and precipitate in another rather than dissolve and precipitate in the same rock volume, estimates to porosity changes would be much greater. With respect to the evaporation to dryness approach, our estimates of the volume of minerals that would form by evaporating Yucca Mountain pore water also show relatively small changes in porosity in the absence of large volumes of water.

In our view, the key question is not simply the magnitude of porosity changes, but the nature of porosity changes and whether small changes in total porosity, perhaps highly localized, may result changes to hydrologic properties significant enough to produce significant EBS performance issues for backfill. The relationship between porosity changes and changes in other hydrologic properties, and the magnitude of changes in hydrologic properties which constitute a significant concern, have not been adequately addressed.

Experiments

General Approach

Thermal-Hydrological Environment - In order to evaluate possible hydrologic property changes induced by thermal-hydrological behavior in the EBS, we need to start with some idea of the thermal-hydrological conditions the backfill would experience. This environment varies with time, space, and the specifics of EBS design, but we believe that a good starting point for assessing coupled thermal-hydrological-chemical effects is consideration of the following environments.

Early in the life of the repository when temperatures are high, the likelihood of seepage into the drift is minimal. Initially, the relative humidity is very low and alteration of backfill material would be expected to be minimal. It may be possible, however, that significant alteration occurs later when the backfill will be subjected to relative humidities above 70% and elevated temperatures.

Therefore, the first environment we consider is backfill at relative humidities above 70% and temperatures that can exceed 100°C.

The second environment occurs when water at elevated but sub-boiling temperatures enters the backfill by either gravity-driven seepage or capillary-driven wicking and flows toward the waste package, and then boils or evaporates as temperatures increase. This seepage flux would most likely be episodic and maximum temperatures would be about 100°C.

We have chosen to conduct two types of experiments to address each of these two environments. To address the first environment, we have designed a crushed tuff batch experiment at above boiling temperatures and high relative humidity. To address the second, we are conducting a sub-boiling two-phase (water vapor and liquid) column experiment. These are described in the "Batch Experiments" and "Column Experiments" sections, respectively, below.

Hydrologic Properties - In these experiments, we are starting with a crushed tuff from the Topopah Spring middle nonlithophysal unit which we received from Alan Flint of the USGS in August 1998. We received several different size fractions from Flint. The extent of chemical reaction of crushed tuff with water and water vapor will depend on the exposed surface area. Since we expect maximum alteration with the finest size fraction material, we have chosen to begin with the smallest fraction, the <2 mm fraction (*SMF Specimen ID 00521699*).

The hydrologic properties of the <2 mm fraction of this crushed tuff were measured by the USGS and reported in a July 31, 1998 USGS memorandum from L. Flint and A. Flint to R. Craig. Bulk density and porosity (ϕ) are reported as 1.37 g/cm^3 and 0.39, respectively. Two sets of moisture retention data were collected using centrifugation, which results in drainage (as opposed to imbibition) capillary pressure versus saturation curves. Based on a fit of these measurements to van Genuchten parameters (*van Genuchten*, 1980), the Flints report values for α and m. The average for the two sets is 470 bars^{-1} and 0.175, respectively. Saturated hydraulic conductivity measurements were reported as "problematic" with a lower limit of 2.5e-4 m/s (equivalent to a saturated permeability, k, of ~2.9e-11 m^2/s).

We chose to wash the fines from this <2 mm fraction in our experiments and use a 1-2 mm fraction derived from this material for our initial experiments. The presence of fines presents several problems. One, the presence of fines impacts our ability to extrapolate our results to other size fractions in some geochemical experiments. As long as the mean particle size is >10 μm, or so, the results of geochemical column experiments are extrapolatable based on total surface area. For very fine particles, this may not be true, owing to their excess surface free energy, which increases both the solubility and dissolution kinetics over that of the bulk material. More importantly, however, the movement of fines with fluid flow can greatly reduce permeability by clogging pore throats.

This was indeed our experience at LLNL. We measured the permeability of the <2 mm fraction of crushed tuff using a 32.5 cm long, 2.5 cm in diameter column. Our measured values are several orders of magnitude lower than those reported by the USGS due to clogging by fines. The USGS measurements were made on a different apparatus (perhaps a shorter column) and evidently did not have the same problem we experienced with fines. For the batch experiments, we also plan to use the 2-4.75 mm fractions of crushed tuff, as well as a well sorted sand with a finer particle size for our initial experiments.

We note that the USGS measurements treat crushed tuff as a single continuum, whereas a dual continuum approach may be more appropriate for modeling. LLNL modeling efforts of backfilled drifts have treated crushed tuff as a dual permeability medium, with the grains as one continuum and the intergranular region as a second continuum, similar to the treatment of fractured tuff where one continuum is the porous matrix and the other is the fracture network.

Based on measured moisture release data (*Peters et al.*, 1984), Topopah Spring tuff will be ~50% saturated at ~95% relative humidity and ~10% saturated at ~80% relative humidity. Even for a low porosity rock at low saturation, for example, Topopah Spring tuff at 10% saturation, the bulk (>99%) of the water in the backfill would be contained within the backfill particles as opposed to on their surfaces. Hence, reaction between adsorbed water and the rock will occur internally as well as externally for porous grains.

Column Experiments

<u>Experimental Design</u>

Our initial column experiment will be a two-phase, sub-boiling version of the single phase plug flow reactor experiments that have already been conducted at LLNL (e.g., *Johnson et al., 1998*). We will loosely pack a 32.5 cm x 2.5 cm diameter column of stainless steel and place it in a convection oven which is maintained at 95°C. The porosity, based on the USGS measurements, is expected to be ~39%. We will pump water at a constant rate using a pump into a diffuser at the bottom of the column. The porous plug at the bottom of the column will force the water to flow up the column. We will control the flow rate so that no liquid water leaves the top of the column. Our aim is to pump as much water as possible through the column with 100% of that water evaporating within column. This rate has been estimated through numerical modeling (see below) and we will confirm the appropriate rate empirically. We start with an air-dry column and increase the flow rate of water until it is just sufficient to exit the column prior to being evaporated. Then we redry the column and use a flow rate just slightly less than this amount. The top of the open column will be maintained at zero (or near-zero) humidity by flowing water-free compressed air over the porous frit capping the top of the column to promote evaporation.

To begin, we will use a water of composition representative of vadose zone pore water at Yucca Mountain, based loosely on analyses presented in *Sonnenthal et al.* (1998). Experiments with a similar water in equilibrium with crushed tuff at 95°C (which will have a higher total dissolved solid load) would provide an upper bound for porosity changes. The initial mineralogical composition of the tuff will be determined using X-ray diffraction (XRD) and post-mortem examination will include XRD, SEM and optical methods. The water permeability of the packed column will be determined prior to starting each run and also at the end of the experiment.

We will monitor the system by continuously recording total flow, and pressure and temperatures at three points along the length of the column. We expect to run the experiment for several months or until back pressure indicated on the pump becomes too great. At the end of the experiment, we will make the post-mortem measurements listed above. In addition, we will rewet some of the evaporite minerals with fresh vadose zone water and analyze the resulting solution to estimate the composition of water that might contact the waste package. Depending on the results of these initial experiments, it might be appropriate to collaborate with Alan Flint of the USGS to design an experimental apparatus such that pre-test and post-test centrifugation analyses could be done on our samples.

Our rationale for this experimental design is as follows. Because we expect that most of the hydrologic property changes in this environment (see earlier discussion of thermal-hydrological backfill environments) will result from mineral precipitation due to evaporation rather than due to water-rock reaction (i.e., dissolution and precipitation in the absence of rapid water removal), we chose a two-phase rather than a single phase design. Rather than begin with a reflux experiment, where both water-rock reaction and evaporation occur, we sought to first isolate the processes of mineral dissolution and precipitation that result from solutes released as the rock dissolves incongruently from those of evaporation at near 100°C, where the continued dissolution of the rock contributes little to the amount of dissolved material present in the water and the precipitation occurs due to rapid removal of water and concentration of the existing solute load. Once we have developed some confidence in our ability to account explicitly and separately for these two processes (mineral dissolution/precipitation and evaporation), we hope to run a full reflux experiment.

Although it is entirely appropriate to accelerate mineral dissolution and precipitation experiments by running them at elevated temperature (being careful to remain within the mineral stability fields appropriate for the temperature of real interest), running accelerated evaporation (two-phase) experiments under pressure (necessary to increase the boiling temperature) can unnecessarily complicate interpretation. This is due to the fact the at increased temperature, water chemistry will change as a function of both dissolution and water removal. The chemistry of water subject to evaporation (water removal) at lower temperature would have little contribution from dissolution. We note that in Rimstidt's reflux experiments, significant changes in mineral precipitation were observed at atmospheric conditions.

We plan to work on the design of full reflux backfill experiments during the next fiscal year. We suggest controlling the acceleration of these reflux experiments through the heat flux used to drive the refluxing, combined possibly with the addition of water with a composition of J-13 well water or other Yucca Mountain pore water to the reflux column, as was done in Rimstidt's experiments (*Rimstidt et al.*, 1989; *Rimstidt and Williamson*, 1991).

Model Predictions

We made calculations of expected porosity changes due to the evaporation of pore water to complete dryness similar to the ones performed by *Zhou et al.* (1996) and arrived at similar estimates for porosity changes. For a J-13-like water, we predict ~0.1 cm^3 of mineral deposition per kg H_20. The total porosity in the column initially is approximately 65 cm^3, therefore at a flow rate of 50 cm^3/day after 60 days, 1.5 mm of column would be completely plugged, or alternatively the porosity over a few centimeters of column would be reduced by a couple of percent. For Yucca Mountain pore waters which have a higher dissolved solute concentration, an equivalent amount of plugging would take less time, scaling approximately with total dissolved solid load.

We also performed thermal-hydrological modeling of this column experiment with the (YMP qualified) NUFT computer code (*Nitao*, 1995). The domain, initial and boundary conditions for these calculations are shown in Fig. 1. Hydrologic properties were based single continuum measurements of the <2 mm fraction of this crushed tuff sent to us by the USGS, as reported in a July 31, 1998 USGS memorandum from L. Flint and A. Flint to R. Craig (α = 470 $bars^{-1}$, m = 0.175, k = 2.9e-11 m^2/s; ϕ = 0.39; See earlier text).

Steady-state temperature, liquid saturation and gas velocity fields for a calculation with 50 cm^3/day are shown in Fig. 2. The temperature drop of a few degrees at the top of the column represents the zone where evaporation is occurring. Note that this region does not extend all the way to the column wall, which is close to the convection oven boundary condition maintained at 95°C. Two-phase conditions exist throughout the top half of the column, with saturation decreasing slightly closer to the column wall. The largest gas velocity vectors are confined to the very top of the column where evaporation is greatest. Temperature fields for injection rates of 1, 50 and 100 cm^3/day^3 are compared in Fig. 3. This figure shows that as the flow rate increases, the evaporation region moves up through the column until the volume of hot, injected water is large enough that two-phase conditions never form.

Results of calculations to examine sensitivity to moisture retention characteristics and permeability are given in Figs. 4 and 5. In the case shown in Fig. 4, the van Genuchten α parameter is varied from 50% less than (4a) to 50% more than (4c) the case shown in Fig. 4b, which is identical to the case shown in Fig. 2. The saturation field is wetter at higher α values, but the system behavior is otherwise very similar. Fig. 5 shows saturation fields for two systems which differ only in the value for saturated permeability (k = 2.9e-14 m^2/s and 2.9e-11 m^2/s). The system with the lower permeability has a wetter saturation field, due to lower air permeability and therefore less efficient evaporation, but the flow and temperature fields are very similar. A flow rate of 25 cm^3/day is used in this example rather than 50 cm^3/day, because at 50 cm^3/day, the lower permeability system becomes too wet and evaporation does not occur. The other system parameters are the same as those shown in Fig. 2. Higher pressures are generated in the lower permeability case, as water is being forced through both columns at the same rate. These model results suggest that the flow rate appropriate for this column experiment is not overly sensitive to the hydrologic properties of the granular material used, and that this rate is well within performance parameters for our equipment.

We also performed coupled thermal-hydrological-chemical calculations with the (non-qualified) chemical version of NUFT. The only aqueous species considered was SiO_2, along with three SiO_2 minerals (crystobalite, quartz and amorphous silica). For a flow rate of 50 cm^3/day, the model predicts a decrease in porosity, not surprisingly, in the driest part of the column which is the top of the column nearest the column wall. The results of a calculation using a starting SiO_2 concentration of 120 ppm by mass at 60 days (Fig. 6) predict a porosity change in the upper few centimeters (the size of the grid cell used in the calculation) of a couple of percent, the same as the prediction based on the evaporation to dryness approach discussed earlier.

Batch Experiments

Our aim is to accelerate potential chemical and physical alteration for backfill under high humidity, above boiling point conditions. To do this, we place backfill samples in an 'aggressive' hydrothermal environment (T= 200 °C; p/p° = 0.94) for several months. The backfill materials are placed in a titanium reaction vessel connected to a reservoir containing a saturated solution of K_2SO_4 (to control relative humidity to 94%) both of which are placed in a convection oven. Initial experiments will use crushed tuff sent by the USGS, both 1-2 mm and 2-4.75 mm fractions, and a well-sorted, fine-grained sand.

We will measure mineralogical and morphological properties of backfill before and after treatment at fixed elevated temperatures and humidities. If significant changes are observed, additional physical measurements (e.g., water sorptive properties) will be made on samples with and without treatment, and subsequent experiments will be initiated to measure the effect of these changes on hydrological and, perhaps, radionuclide transport properties using column and centrifuge techniques. Long-term tests at lower temperatures and lower relative vapor pressures may also be indicated if significant effects are noted in the initial series of experiments.

Based on our earlier discussion of alteration of crushed tuff, we would expect that alteration products if formed in these batch experiments, would be zeolites (clinoptilolite, dachiardite, mordenite), clay minerals (smectite, illite), calcite, and potentially a silica phase (cristobalite). Any of these phases, if precipitated at grain contacts could affect the transport and mechanical properties of the backfill. Formation of clay minerals and zeolites could also significantly affect the radionuclide-sorptive properties of the backfill, and depending on the specific radionuclide, significantly increase retardation. We predict, however, that changes to inter-particle porosity and intra-particle porosity for both the crushed tuff and the sand, if any, will be extremely minor.

The following summarizes the key activities that will be undertaken. Details of experimental protocol that are being considered are given in an appendix.

1. Preliminary experiments to assess the physical and chemical changes in backfill materials treated under an 'aggressive' hydrothermal environment (T= 200 °C; $p/p^{\circ} = 0.94$).
    a) Characterize samples prior to hydrothermal treatment.
        i) Characterize backfill mineralogy using qualitative and quantitative X-ray analysis.
        ii) Characterize backfill morphology using optical and scanning electron microscopy.
    b) Hydrothermally treat backfill samples.
        i) Samples of backfill appropriate for subsequent physical and chemical characterization will be placed in reaction vessels that are connected to a reservoir containing a saturated solution of K_2SO_4.
        ii) The reaction vessels and attached reservoirs will be placed in convection ovens and maintained at 200 °C.
        iii) After an interval of at least 3 months, but less than 6 months, backfill samples will be removed from the reaction vessels.
    c) Characterize samples subsequent to hydrothermal treatment using the techniques listed above.
    d) Based on the results of the post-treatment characterization determine whether the additional work is warranted (further hydrothermal treatment, additional physical and chemical properties measurements, additional experiments to assess the effects of the treatment on hydrological properties)
    e) Repeat b.iii. and c. and d. as necessary.
2. If alteration of backfill is deemed significant, make additional measurements and undertake experiments to assess the hydrological changes in backfill materials treated under an 'aggressive' hydrothermal environment.
    a) Characterize the backfill water sorptive properties by measuring water sorption at fixed values of p/p°.
    b) Characterize backfill radionuclide sorptive properties using batch tests to determine sorption isotherms.

c) Characterize the unsaturated hydraulic conductivity of the backfill using an ultracentrifuge.

   i) Construct sample holders for unsaturated conductivity measurements that can withstand the temperature, pressure, and p/p° of the hydrothermal treatment.

   ii) Measure unsaturated hydraulic conductivity at USGS-Sacramento laboratory.

d) Characterize the radionuclide transport properties using columns of backfill. Measure the breakthrough under saturated conditions of a conservative tracer and two sorbing tracers through chromatography columns filled with samples of backfill.

e) Treat the samples used for unsaturated hydraulic conductivity and samples used for transport tests at 200 °C and p/p°=0.94 for a period defined by the initial experimental results.

f) Remove samples from reaction vessels and repeat unsaturated hydraulic conductivity tests and radionuclide transport experiments.

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References

Abrajano T. A., Bates J. K., and Byers C. D. (1986), Aqueous Corrosion of Natural and Nuclear Waste Glasses .I. Comparative rates of hydration in liquid and vapor environments at elevated-temperatures. Journal of Non-Crystalline Solids 84, 251-257.

Abrajano T. A., Bates J. K., and Mazer J. J. (1989), Aqueous corrosion of natural and nuclear waste glasses: II. Mechanisms of vapor hydration of nuclear waste glasses. Journal of Non-Crystalline Solids 108, 269-288.

Abrajano T. A., Bates J. K., Woodland A. B., Bradley J. P., and Bourcier W. L. (1990), Secondary phase formation during nuclear waste-glass dissolution. Clays and Clay Minerals 38, 537-548.

Bruton C. J. and Viani B. E. (1992), Geochemical modeling of water-rock interactions in the unsaturated zone. 7th International Symposium on Water-Rock Interaction -- WRI-7, (eds Y. K. Kharaka and A. S. Maest), Vol. 1 , pp. 705-708. A.A. Balkema.

Delany, J. M. (1985), *Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Modeling Code*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53631.

Fyfe D. (1976), The atmosphere. In Corrosion: Metal/Environment Reactions, (ed L. L. Shreir), Vol. 1., pp. 2:26-37. Butterworths, London.

Harrar, J. E., J. F. Carley, W. F. Isherwood, and E. Raber (1990), *Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-21867. (NNA.910131.0274)

Ho, C. K. and S. W. Webb (1998), Capillary barrier performance in heterogeneous porous media, Water Resources Research 24, 603-609.

Holmes H. F. and Mesmer R. E. (1986), Isopiestic studies of aqueous solutions at elevated temperatures VIII. The alkali-metal sulfates. Journal of Chemical Thermodynamics 18, 263-275.

Johnson, J. W., K. G. Knauss, W. E. Glassley, Laura D. DeLoach and A.F.B. Tomson, Reactive transport modeling of plug-flow reactor experiments: quartz and tuff dissolution at 240 C, in press J. Hydrology.

Knauss K. G. and Beiriger W. B. (1984), Report on Static Hydrothermal Alteration Studies of Topopah Spring Tuff Wafers in J-13 Water at 150°C. Lawrence Livermore National Laboratory, UCRL-53576, Livermore, CA 94550.

Knauss, K. G., W. J. Beiriger, and D. W. Peifer (1987), *Hydrothermal Interaction of Solid Wafers of Topopah Spring Tuff with J-13 Water and Distilled Water at 90 and 150°C Using Dickson-Type,* *Gold-Bag Rocking Autoclaves: Long-Term Experiments*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53722. (NNA.19870713.0081)

Knauss, K. G., W. J. Beiriger, D. W. Peifer, and Piwinski, A. J. (1985), *Hydrothermal Interaction of Solid Wafers of Topopah Spring Tuff with J-13 and Distilled Water at 90°, 150° and 250°C Using Dickson-Type, Gold-Bag Rocking Autoclaves*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53645.

Linke W. F. and Seidell A. (1965), Solubilities: Inorganic and Metal Organic Compounds. American Chemical Society, Washington, D.C.

Nitao, J.J. (1995), Reference manual for the NUFT flow and transport code, Version 1.0. Livermore, CA: Lawrence Livermore National Laboratory. (UCRL-IC-113520).

Oldenburg, C. M. and Pruess, K. (1993), On numerical modeling of capillary barriers Water Resources Research 29, 1045-1056.

Papadakis V. G., Vayenas C. G., and Fardis M. N. (1991), Experimental investigation and mathematical modeling of the concrete carbonation problem. Chemical Engineering Science 46, 1333-1338.

Rimstidt, J. D. and M. A. Williamson (1991), Vertical thermal gradient experiment results, report to Mifflin and Associates.

Rimstidt, J.D., W.D. Newcomb, and J.L. Shettel Jr. (1989), "A vertical thermal gradient experiment to simulate conditions in vapor dominated geothermal systems, epithermal gold deposits, and high level radioactive repositories in unsaturated media." In proceedings from *Water-Rock Interaction.* Rotterdam. A.A. Balkema. 6:585–588. (D.L. Miles [ed.]).Jenkins et al., 1984.

Roberts S. and Viani B. E. (1998), Determination of Mineral Abundances in Samples from the Exploratory Studies Facility, Yucca Mountain, Nevada, Using X-Ray Diffraction. Lawrence Livermore National Laboratory, UCRL-ID-129748, Livermore, CA 94550.

Ross, B. (1990), The diversion capacity of capillary barriers, Water Resources Research 26, 2625-2629.

Sonnenthal, E., N. Spycher, J. Aps and A. Simmons (1998), Thermo-Hydro-Chemical Predictive Analysis for the Drift-Scale Heater Test, Lawrence Berkeley National Laboratory report, YMP Level 4 Milestone SPY289M4.

Steefel, C.I., and S.B. Yabusaki (1995),. "OS3D/GIMRT: Software for modeling multicomponent-multidimensional reactive transport." Richland, WA: Pacific Northwest Laboratory, Battelle Memorial Institute.

van Genuchten, M.Th. (1980), A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Science Society of America Journal 44*, 892-898.

Viani B. E. and Torretto P. C. (1998), Sorption and Transport of Uranium on Hematite. Lawrence Livermore National Laboratory, UCRL-ID-129848, Livermore, CA 94550 (YMP Milestone Report SPL3BM4 - 1997).

Warren, R. S., F. M. Byers, and F. A. Caporuscio (1984), *Petrography and Mineral Chemistry of Units of the Topopah Spring, Calico Hills, and Crater Flat Tuffs, and Older Volcanic Units, with Emphasis on the Samples from Drill Hole USW G-1, Yucca Mountain, Nevada Test Site*, Los Alamos National Laboratory, Los Alamos, NM, LA-10003-MS. (HQS.19880517.2569)

Wolery, T. J. (1992), *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-MA-110662.

Zhou, W., J. Conca, R. Arthur, M. Apted (1996), Analysis and Confirmation of Robust Performance for the Flow Diversion Barrier System within the Yucca Mountain Site, Report prepared for Electric Power Research Institute TR-107189; 3294-17, Final Report December 1996.

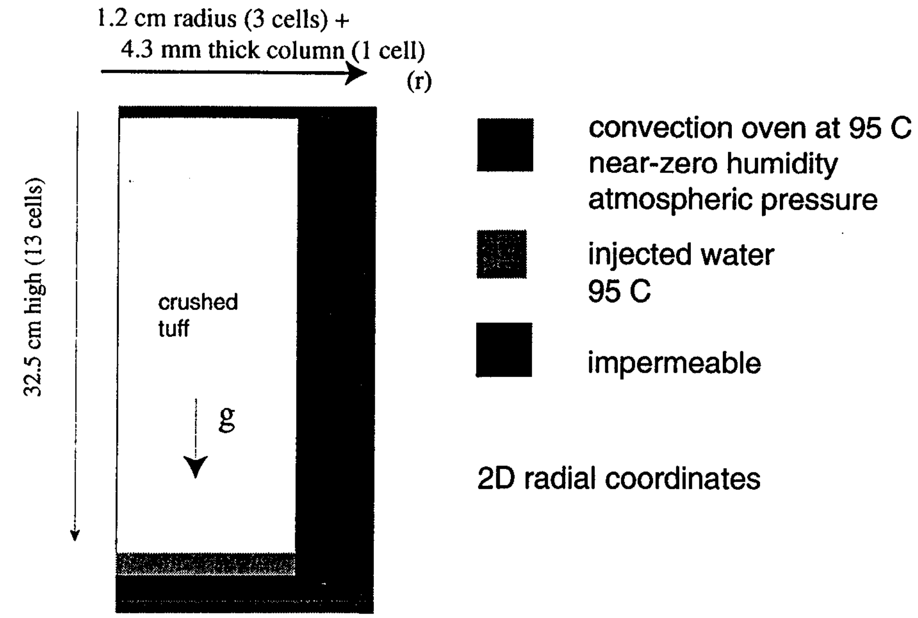


Fig 1. Set-up for NUFT modeling of column experiments.

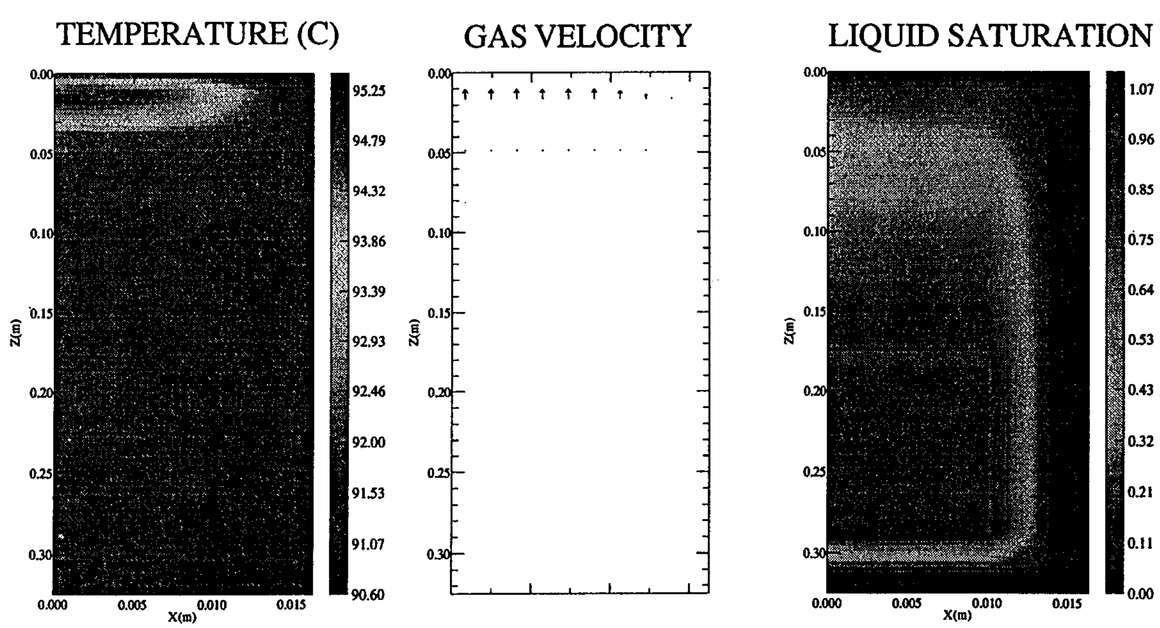


Fig. 2. Temperature, gas velocity and liquid saturation fields for simulation of column experiment. Injection rate is 50 cc/day. Saturated liquid permeability = 2.9e-11 m^2/s, $\alpha = 470$ $bars^{-1}$, m = 0.175, $\phi = 0.39$.

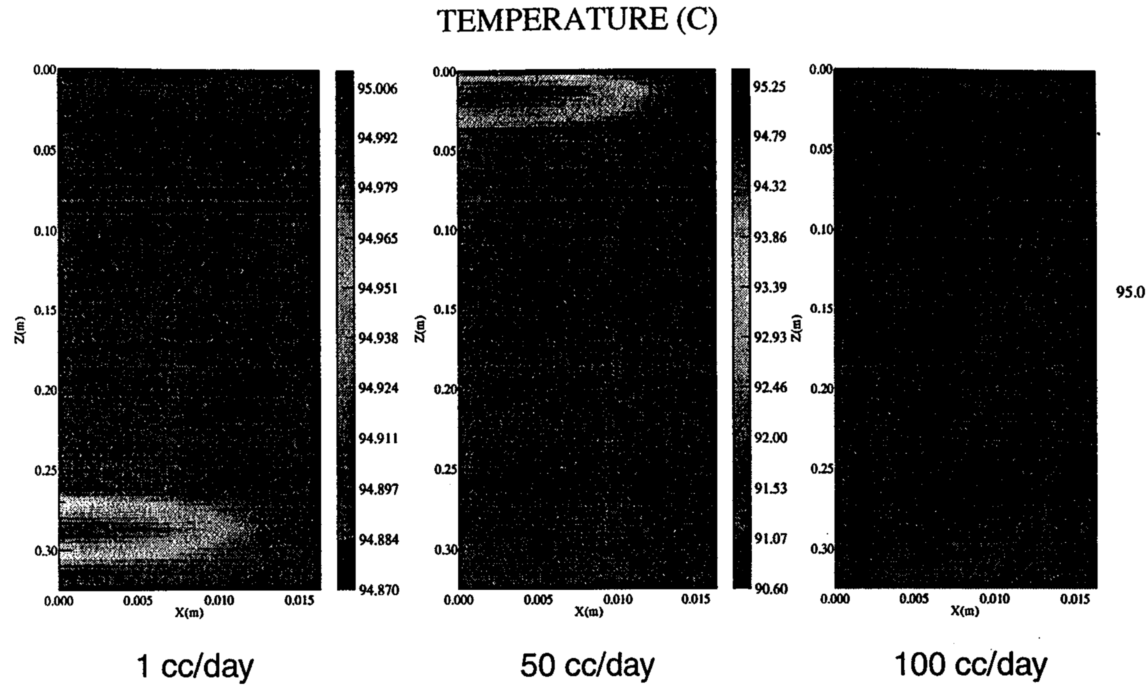


Fig. 3. Temperature fields from simulations of column experiment for a variety of injection rates. Saturated liquid permeability = 2.9e-11 m^2/s, $\alpha = 470$ $bars^{-1}$, m = 0.175, $\phi = 0.39$.

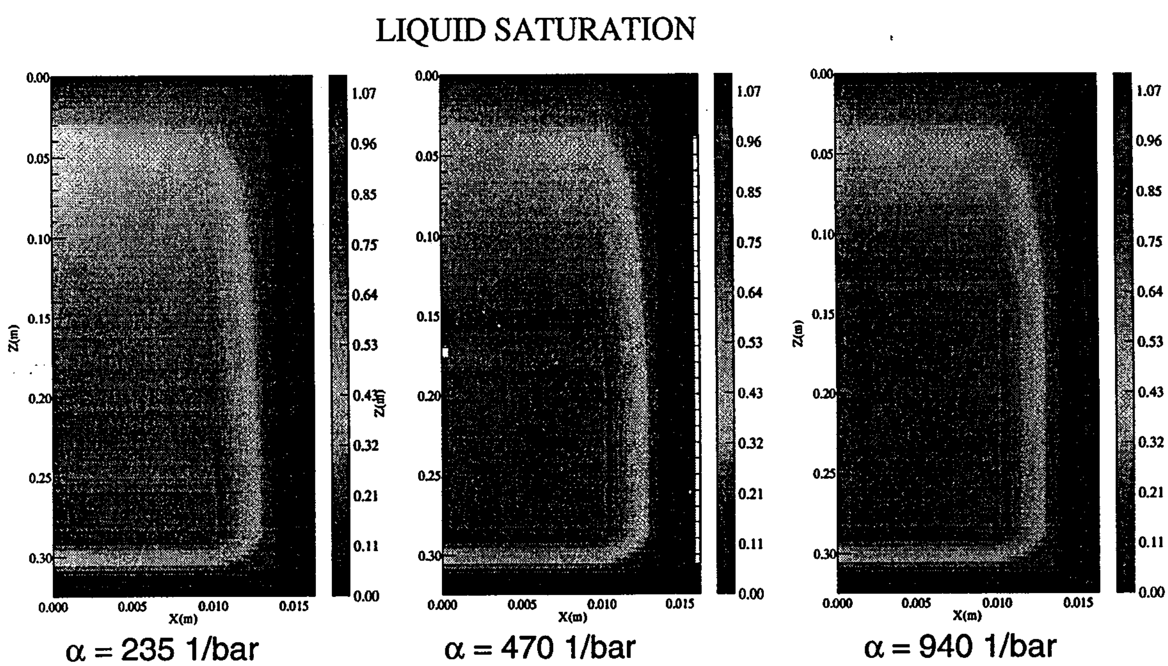


Fig. 4. Saturation fields from simulations of column experiment for an injection rate of 50 cc/day for a variety of van Genuchten α values. Saturated liquid permeability = 2.9e-11 m^2/s, m = 0.175, $\phi = 0.39$.

LIQUID SATURATION

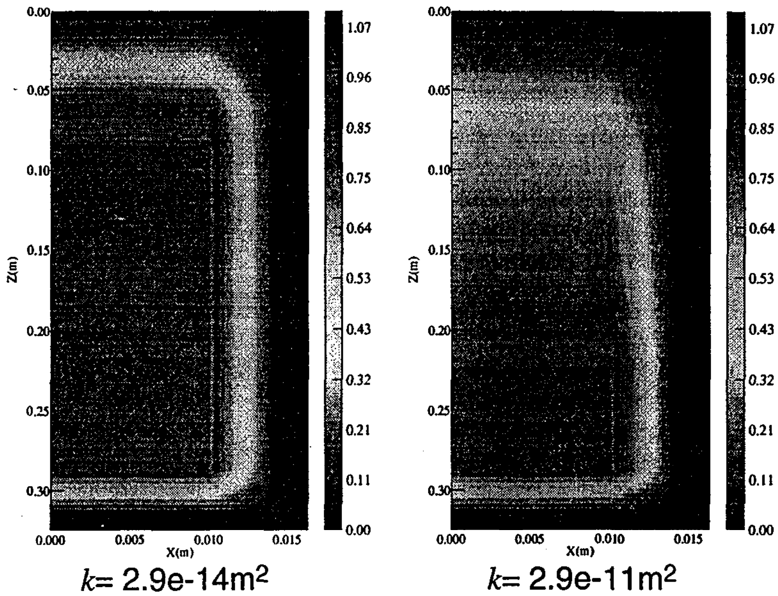


Fig. 5. Saturation fields from simulations of column experiment for an njection rate of 25 cc/day for two different permeablity values. $\alpha = 470$ bars^{-1}, m = 0.175, $\phi = 0.39$.

RATIO POROSITY CHANGE

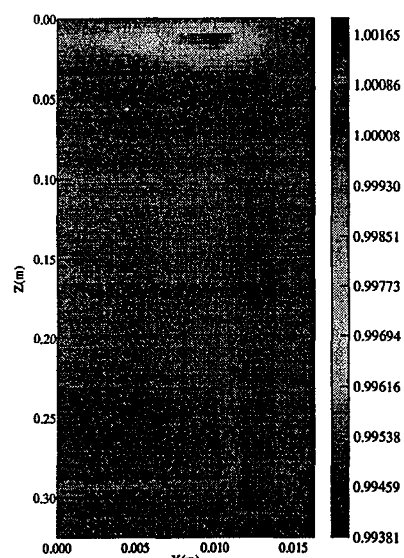
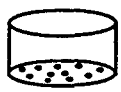
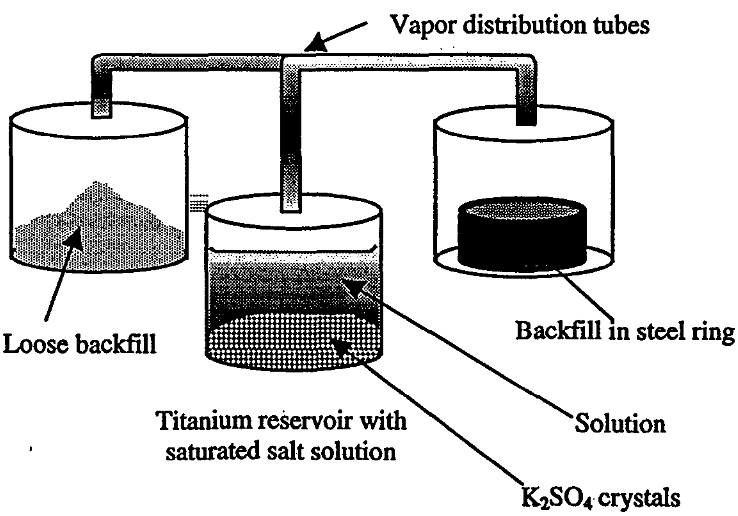
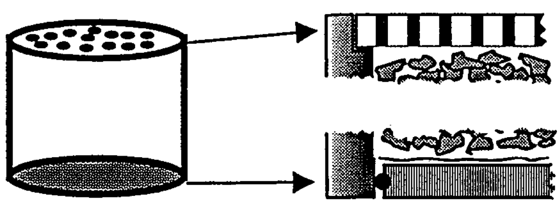


Fig. 6. Ratio of porosity change for simulation of column experiment for an injection rate of 50 cc/day. Saturated liquid permeability = 2.9e-11 m^2/s, $\alpha = 470$ bars^{-1}, m = 0.175, ϕ (initial) = 0.39.

APPENDIX

Activity	Protocol
1.a.i.	Quantitative bulk mineralogy – 1-2 g samples will be ground in a vibrating ball mill to reduce particle size to approximately 10 μm or less. Subsamples containing > 200 mg will be mixed with corundum in the ratio of 4:1. These samples will be loaded into a 13x25-mm side mount sample holder and X-rayed. The resulting X-ray patterns will be analyzed using the Reitveld method to estimate mineral abundances (Roberts and Viani, 1998). Clay mineralogy – 2-4 g samples will be mixed with dilute NaCl solution and contacted with an ultrasonic probe for 2-10 minutes. The resulting mixture will be centrifuged to sediment the > 2 μm e.s.d. fraction. The supernatant containing the < 2 μm e.s.d. will be sedimented on a zero-background quartz plate and X-rayed after air-drying and after solvation with ethylene glycol. The resulting X-ray patterns will be analyzed to identify the clay-sized phases.
1.a.ii.	Optical and SEM morphology – Samples of the backfill will be loaded into 12-25x ~10 mm I.D. stainless steel cylinders with a bottom of stainless and/or carbon steel drilled with drain holes. The samples contained in the cylinders will be examined using reflected light microscopy and by SEM after coating with carbon. Replicates of each sample will be embedded in epoxy, ground, polished, and examined by SEM. Thin sections of the epoxy embedded samples may be fabricated and used for transmitted light microscopic analysis. Images of the SEM and optical analyses will be taken. Qualitative elemental analysis of individual mineral grains may be made using the energy dispersive X-ray analysis capability of the SEM.  h = ~ 10-15 mm d = 12-25 mm
1.b.i.	Reaction chambers for thermal treatment – The samples used for X-ray, microscopic, tracer sorption, and water sorption analyses will be placed in reaction bombs that are connected to a reservoir containing a mixture of K_2SO_4 crystals (arcanite) and a solution in equilibrium with it. Titanium vessels will be used for the saturated solution reservoirs; titanium, hastelloy, and/or stainless steel will be used for the backfill reaction vessels. Vapor tubes connecting the reservoirs will be stainless steel and will be bent (looped) to prevent any of the salt solution from contacting the sample. The reservoir will be partially filled with a mixture of water and K_2SO_4. The mass ratio of K_2SO_4 to water will be greater than 26::74, the solubility of K_2SO_4 at 208 °C (Linke and Seidell, 1965). The solubility data of Linke and Seidell (1965) was used together with the osmotic coefficients of Holmes and Mesmer (1986) to compute the equilibrium relative vapor pressure of a saturated solution of K_2SO_4 at 200 °C ($p/p°$ 0.945). 

Activity	Protocol
1.b.ii.	The saturated salt solution reservoir and reaction chambers will be placed in a convection oven which will be slowly (~ 5 °C/h) brought to temperature.
1.b.iii.	At intervals, either the entire reaction chamber system, or specific reaction chambers, will be removed from the oven and slowly cooled to room temperature.
1.c.	Characterize the backfill samples as described in 1.a.i--1.a.ii
2.a.	Water adsorption – 2-5 g samples will be dried at 70 °C, weighed and placed in chambers above saturated salt solutions that control the relative vapor pressure ($p/p°$). The mass of water adsorbed at these fixed relative humidities will be measured by re-weighing the samples after equilibration.
2.b.	Sorption isotherms – 1-2 g samples will be mixed with an appropriate volume (e.g., 25 mL) of a dilute (e.g. 0.01 N) NaCl solution containing a known quantity of a sorbing tracer. Tracer concentrations will be varied over an appropriate range. The samples will be mixed periodically and the supernatants will be sampled, filtered, and analyzed after equilibration times of ~2 days and ~1 week. The resulting data will be used to calculate sorption isotherms and partition coefficients. Tracers that will be considered are U, Np, and NH_4^+. Analysis of U and Np will be by alpha scintillation spectrometry. NH_4^+ will be analyzed by specific ion electrode.
2.c.i.	Construct unsaturated flow cell – Stainless steel sample holders with dimensions and construction details required for use with the ultracentrifuge used by the USGS – Sacramento to measure unsaturated hydraulic conductivity (Flint and Flint, 1998) will be fabricated in pairs.  OD – 50.80 – 50.85 mm height – 62.7 mm mass of matched pairs within 0.1 g The device will consist of a cylinder with a top (inner) cover containing holes to distribute water to the sample, and a bottom (outer) support containing finer holes to prevent fines from being produced and/or support a filter paper.
2.c.ii.	The unsaturated flow test cell will be loaded with sample, transported to the USGS-Sacramento facility, where unsaturated hydraulic conductivity will be measured. Subsequent to those measurements, the cells with samples will be transported back to LLNL for hydrothermal treatment.
2.d.	Radionuclide and conservative tracers will be used to measure the transport properties of the backfill material using column studies similar to those used by Viani and Torretto (1998).
2.e.	See 1.b
2.f.	See 2.c. and 2.d.